Ultra-low-κ polyimide hybrid films via copolymerization of polyimide and polyoxometalates†

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Novel polyimide hybrid films in which nanoscale polyoxometalates (POM) clusters are covalently linked with the polymer chains exhibit not only drastically reduced dielectric constants relative to neat polyimide film, as low as 1.22, but also improved thermal stability, and mechanical properties without sacrificing the transparency of the polymer films.

The interest in hybrid materials lies in their appealing properties, which result from the possibility to combine inorganic, organic, and biological functions in a tailored matrix or nanocomposite.1,2 In particular, organic–inorganic hybrid materials have attracted remarkable attention for microelectronics and end use because their utilization in integrated circuits can lower line-to-line noise in interconnects, and alleviate power dissipation issues by reducing the capacitance between the interconnection conductor lines.3,4 Although a great deal of effort has been made, it is still a considerable challenge to find an alternative to traditional insulators like silicon dioxide for future devices.5,6 In view of the dielectric constant of air (κ = 1.01), the introduction of controlled porosity in materials, typically with pore sizes well below the smallest device features, 10 Å or less, has been envisioned as a promising method for developing ultra-low dielectric materials.7,9 As an example, Lee et al. demonstrated the preparation of an ultra-low dielectric organosilicate film (polymethylsilsesquioxane, PMSSQ), where ethyl acrylate-terminated polypropyleneimine dendrimers were used as a porogen to yield narrow-distributed, closed spherical pores of radius <2.0 nm.8 As the porosity of the films increased by 32%, their κ value was decreased by 1.6.9 However, the mechanical strength of the resulting nanoporous film is weak and the Young’s modulus is only 0.6 GPa.

Polyimides are well known for their excellent mechanical properties and high-temperature durability and have been used as interlayer dielectrics in microelectronics by simple spin-coating techniques.10 To balance their mechanical properties and dielectric constant, porous nanoparticles with stiff structures are attracting more attention. For example, porous polyhedral oligomeric silsesquioxane (POSS)10,11 and silica nanotubes12 have been used in attempts to achieve simultaneous improvements in the mechanical and dielectric properties of polyimide films.

Polyoxometalates (POM) are also porous inorganic nanoparticles or molecular clusters and have found wide applications in many fields.13 As nanobuilding blocks, they have been embedded into some polymers and resulted in pronounced property improvements of the resulting materials.14,15 Due to the structural resemblance to semiconductor materials they have been used to fabricate composite materials for molecular switching devices.14 This inspired us to explore the possibility of improving the dielectric properties of polyimides by incorporating organically modified POM clusters.

The POM cluster used in this work is a highly nucleophilic divacant lacunary decatungstosilicate with chemical formula K_8[\gamma-SiW_{10}O_{36}]_3\cdot12\text{H}_2\text{O}, synthesized following a procedure developed by Tezé et al.15 In the present work, to carry out the copolymerization of POM clusters with pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA), two amine groups were attached to the lacunae of each tungstosilicate cluster by reaction with γ-aminopropyltriethoxysilane. A representative synthesis procedure for polyimide/POM hybrids is illustrated in Scheme 1. Details of the experimental preparation and characterization for the organically modified POM and the hybrid films can be found in the electronic supplementary information (ESI).†

The dynamic mechanical behavior of the polyimide and its hybrid films with different POM contents is shown in Fig. 1. All the measurements were performed in the temperature range 70–400 °C with a frequency of 0.1 Hz and a fixed sample size. The tensile modulus at 75 °C (below T_g) for the neat polyimide film is about 1.6 GPa (see Fig. 1a). The incorporation of POM clusters efficiently increases the storage modulus E’ of these polyimide films. For example, E’ at 75 °C for the 10 wt% POM hybrid film increased to 3.4 GPa, an increase of 110% compared to that of the neat polyimide film. With increasing temperature, E’ of the hybrid film decreases but not very much, and is still 700 MPa even at 390 °C. In contrast, E’ of the neat polyimide film drastically decreases, especially starting from 300 °C, and is only 24.5 MPa at 390 °C. Such a reinforcing effect can be attributed to the increasing stiffness of main chain in the polyimide containing POM clusters. The incorporated POM clusters elevate the activating threshold of segmental motion and reduce the response rate to the applied stress, which can be further verified from the change in glass transition temperature T_g of the films.

The loss factor tan δ curves in Fig. 1(b) reveal a pronounced increase in T_g, defined as the peak temperature in the tan δ curves, as high as 66 °C (from 317 to 383 °C) as the POM content in polyimide films is increased by 10 wt%. Furthermore, the peak width of tan δ during the primary transition becomes broader with increasing POM content. Generally, the glass transition temperatures of polymers reflect their segmental mobility, especially when
the involved samples experience an identical thermal history. As a consequence, both the elevated $T_g$s and broadened transition regions with increasing POM content indicate that there exist strong interactions between the clusters and the matrix, which confine the segmental motion of the polyimides.

Thermal stability of polymer films is vital to their application in microelectronics. The annealing step during the microchip fabrication is required to ensure void free copper deposits, and is usually performed in a temperature range of 400–450 °C for up to 1 h. To examine the thermal durability of these hybrid films, several thermogravimetric (TGA) experiments were performed under N$_2$ atmosphere. It was found that the initial decomposition temperature $T_d$, defined as 5% weight loss, significantly increases with increasing POM content, and a $T_d$ increase of 32–46 °C for all the hybrid films can be observed. The detailed TGA results and the possible explanation for the improved thermal stability are presented in ESI.

The $k$ values of all the films are shown in Fig. 2. It is found that the $k$ of the neat polyimide film at 1 MHz is 3.49 and agrees well with the result reported by Liang et al., where a 51 μm thick standing PMDA–ODA film was used. As the POM content increases, $k$ of the polyimide hybrid films remarkably decreases and even reaches 1.22 for the 10 wt% sample. In a recent work, Gross et al. also observed a similar improvement in PMMA hybrid films containing zirconium oxoclusters, where the $k$ value of PMMA films with 20 wt% Zr$_2$O$_2$(OMc)$_{12}$ clusters was reduced to 1.93 from 3.0 for the neat film.

As mentioned previously, increasing free volume facilitates the lowering of the dielectric constant of materials. It has been well recognized that the addition of inorganic components can result in loose stacking of the macromolecules surrounding the solid particles. For instance, 18 mol% of POSS makes the relative porosity of polyimide hybrid films increase by 6.8% on the basis of the calculation in density variation. Fig. 3 shows scanning electron microscopy (SEM) photographs of the fracture surfaces of the polyimide–POM hybrid films. It can be seen that the surface protuberances resulting from the POM clusters are homogeneously distributed in the whole film, and the number of protuberances increases with increasing POM content, to some extent reflecting the increased free volume in these hybrid films. However, the increasing free volume seems not to be the only reason leading to the reduction in the dielectric constants of hybrid films. If the hybrid film is envisioned as a simple two-phase system, it will need porosity as high as 90% or more to reach the present $k$ value (1.22), in terms of prediction of the Bruggeman effective medium approximation. This is quite difficult to achieve such a porosity only by incorporating POM.

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POM clusters consist of smaller nanocrystallites, which construct many micropores or continuous voids between crystallites and consequently a large interface. When they are embedded into polymer matrices, the resulting heterostructure is likely to exhibit remarkable changes in dielectric properties. The dielectric confinement arising from such heterostructures has a pronounced influence on the optical and transport properties of materials, which has been the subject of recent theoretical and experimental research. Both smaller crystallite size and increased interface within the hybrids result in a strong self-polarization-induced radial localization of electronic density at the heterojunction, and thus reduce the $k$ of the materials. In addition, it has been shown that the charging energies of polyoxometalates are in the range...
0.1–4.0 eV and the resolution of discrete electronic levels at room temperature is thus expected. The trapped electron and charge confinement increase the binding energy of the hybrid films and thus reduce the size-dependent static dielectric constant.24 Apparently, the specific heterostructure and the induced variations in polarization effect and binding energy are also likely to be responsible for the prominently decreased \( k \) in the hybrid films.

In summary, a convenient route to the fabrication of polyimide hybrid films with ultra-low dielectric constant \( (\kappa = 1.22) \) has been proposed. On the basis of a simple copolymerization, the organically modified POM clusters are covalently incorporated into polyimide chains, and significantly improve the thermal and mechanical properties of the polymer films without sacrificing their optical transparency. This method can be extended to other polyoxometalate clusters and polymers and thus opens a new approach to develop ultra-low \( k \) hybrids or other functional materials.

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Notes and references


